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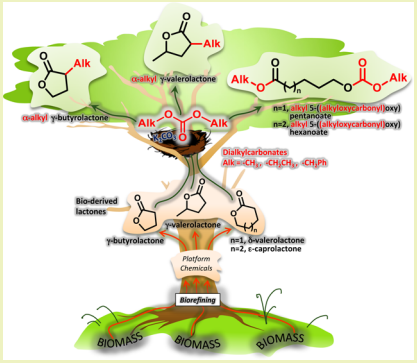
Upgrading of Biobased Lactones with Dialkylcarbonates

Alessio Caretto, Marco Noè, Maurizio Selva, and Alvise Perosa*

Dipartimento di Scienze Molecolari e Nanosistemi, Centro per le Tecnologie Sostenibili, Università Ca' Foscari Venezia, Dorsoduro 2137 − 30123 Venezia, Italy

Supporting Information

ABSTRACT: Four renewable lactones, γ-butyrolactone, γ-valerolactone, δ-valerolactone, and ε-caprolactone (GBL, GVL, DVL, ECL, respectively) were shown to react with dimethyl-, diethyl-, and dibenzyl-carbonate (DMC, DEC, DBnC, respectively) in the presence of K_2CO_3 as basic catalyst, to yield selectively either the α-alkyl derivatives **1c−6c** in the case of the five-membered ring GBL and GVL or the highly oxygenated acyclic monomeric derivatives **7a**, **8a**, and **9a** in the case of the six- and seven-membered rings DVL and ECL. Selectivity and reaction conditions are investigated and a reaction mechanism is proposed. The organic carbonates act both as reagent and as reaction solvents, and the catalyst can be recovered by filtration and recycled.



KEYWORDS: *Butyrolactone, Valerolactone, Caprolactone, Dimethylcarbonate, Diethylcarbonate, Dibenzylcarbonate*

INTRODUCTION

The efficient production of biobased chemicals is an indispensable component for the growth of the biorefining industry. Currently, the choice of products derived from renewable substrates, as well as the development of novel conversion technologies to synthesize them, is still one of the bottlenecks toward a fully integrated biorefining industry.[1] In particular, the transformation of biobased platform chemicals suffers from a limited plethora of available conversion technologies. Conversely, it provides access to a potentially huge number of targets, some are analogous to those used by the petrochemical industry,[2] but many are new and yet unexplored biorefinery intermediates. Past experience of the chemical industry indicates that this complexity can be handled by using broad-based technologies—often catalytic (selective reductions and oxidations, bond making/breaking processes, catalysis, etc.)—to produce multiple outputs, as opposed to a "like-for-like" target-based approach aimed at replacing well-established chemicals produced from fossil feedstocks. We have already described approaches to this broad-based strategy toward the development of new chemistry and, in the longer term, a plethora of new chemicals.[3−5] Now, we have focused our attention on the catalytic transformation of renewable biobased lactones.

Current advances of research on the synthesis of biorefinery-derived chemicals have demonstrated that useful lactones can be obtained from biomass (Figure 1). For example, γ-butyrolactone (GBL) can originate reductively[6−8] from succinic acid (Figure 2), that is one of the most promising biobased chemicals[1,6,9,10] obtainable from glucose via a fermentative[11−15] pathway. GBL has recently been subject of widespread interest as solvent and intermediate.

γ-Valerolactone (GVL) is directly obtainable in high yields by hydrogenation of levulinic acid (LA) (Figure 1).[6] The latter is one of the main platform chemicals obtained from the chemical transformation (acidic digestion) of cellulose and hemicelluloses. Processes for its production have already been patented,[16−19] proving also the economic feasibility of the whole transformation. This fact, together with the ease of LA lactonisation[4,20] has made GVL the most promising lactone obtainable from biomass. GVL research was addressed to its possible use for the production of biofuels[20,21] (valeric biofuels) and new solvents,[22] making it a hot topic of study.

The production of six-membered ring δ-valerolactone (DVL) from biomass is still not as studied as GBL and GVL. However, it is likely to become of greater interest, given its well-known use as a monomer.[23−27] One of the biobased production processes starts from furfural (another platform chemical, obtained from acidic treatment of pentoses) by reduction to tetrahydrofurfural, followed by ring-expansion to DVL by means of an *N*-heterocyclic carbene (Figure 3).[28]

Another possible pathway to DVL involves reduction of glutamic acid to 1,5-pentanediol.[6] The latter can then undergo oxidation and lactonization, as described in a recent paper.[29]

Finally, it was recently demonstrated that also ECL can be obtained by a biobased route starting from hydroxymethylfurfural (HMF) in four steps, involving as intermediates 2,5-THF-dimethanol (THFDM), 1,2,6-hexanetriol (1,2,6-HT), and 1,6-hexanediol (1,6-HD).[30]

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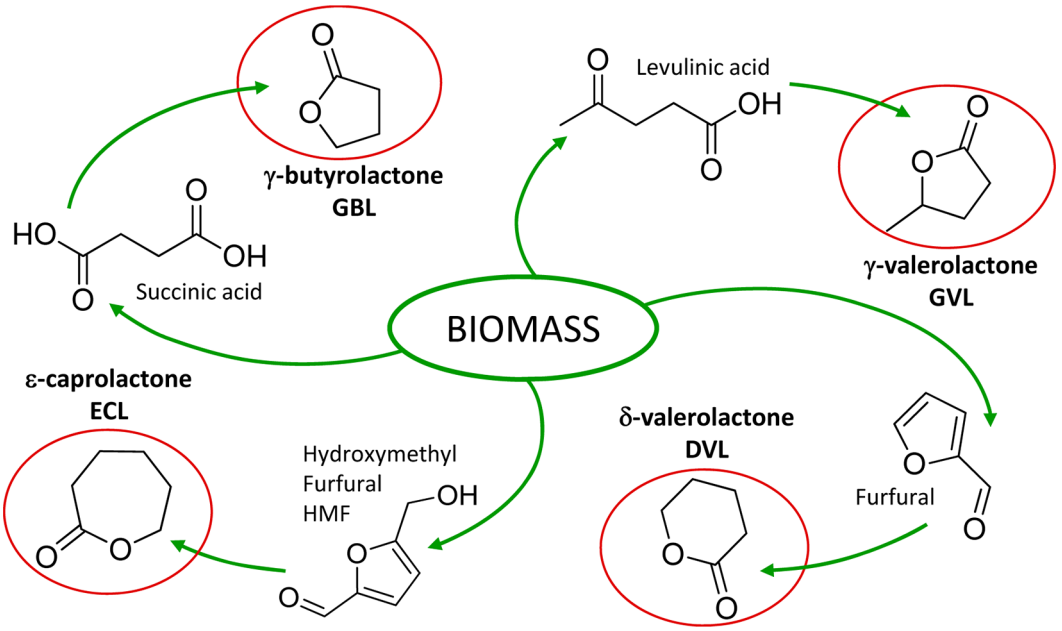


Figure 1. Biobased lactones.

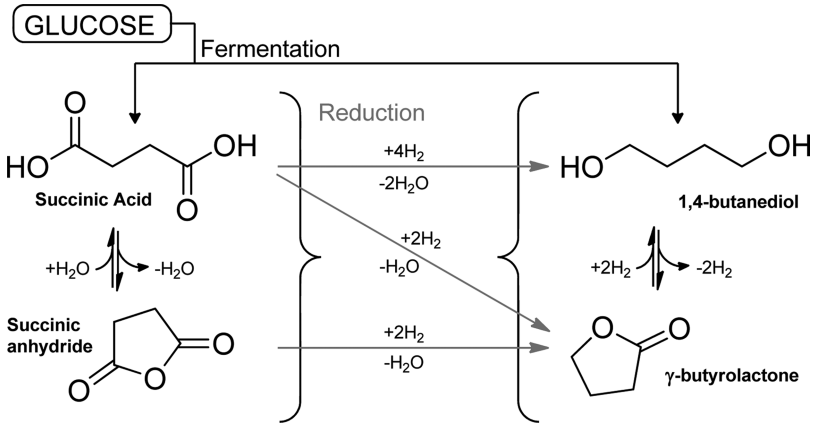


Figure 2. γ-Butyrolactone (GBL) from succinic acid.

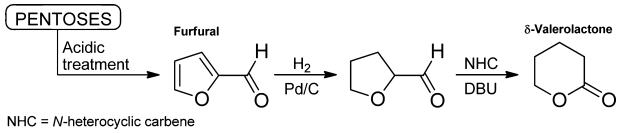


Figure 3. Biobased synthesis of δ-valerolactone.

Lactone structures are often present in natural compounds and bio active molecules,[31] such as sesquiterpene lactones[32] and some lignans[33] (Figure 4, left), and as a consequence, their structure appears in many drugs (such as macrolides used as antibiotics[34] and anticancer agents[35]) as well. For these reasons they have been the subject of fundamental as well as applied chemical research, the latter concerning especially polymers (Figure 4, right). Worth citing here are γ-butyrolactone, commonly used as a solvent or precursor for synthesis, and ε-caprolactone, widely used in the production of polymers.[36] The derivatization of lactones has played and still plays an important role in the broadening of their possible uses.

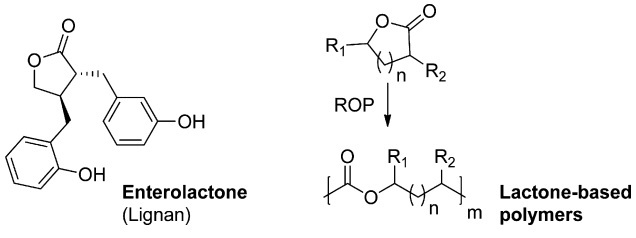
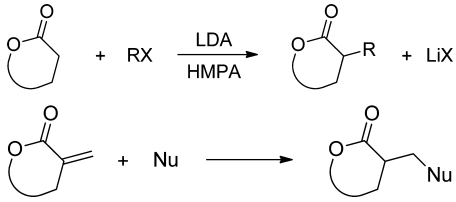


Figure 4. Examples of bioactive lactones.

Alpha-alkylation is one of the common methods used to modify lactones, it seldom makes use of catalytic technologies, and it generally involves the use of undesirable chemicals (dangerous to handle as well as for health and the environment) such as alkyl halides (Scheme 1, top)[37] and alkyl sulfates, as well as of bases (generally lithium and potassium salts of organic bases[38,39]), whose use generates stoichiometric amounts of unwanted salts.

A catalytic method used to obtain alpha-alkyl derivatives of lactones starts from the corresponding alpha-alkylidenes which are reacted with a suitable nucleophile (generated in situ) in a Michael reaction (Scheme 1, bottom). However, the production of alkylidenes from the corresponding lactones is

Scheme 1. Synthetic Strategies Towards Alpha-alkyl Lactones



generally not straightforward, due to the necessity of catalysts which are prone to deactivation.[40,41]

An alternative greener methylation reagent was shown to be dimethylcarbonate (DMC), that acts as alkylating agent for several nucleophiles, including alcohols, amines, and CH_2-active compounds under catalytic conditions.[42] In 1991 a preliminary report indicated that α-methyl-γ-butyrolactone was formed in the base-catalyzed reaction of γ-butyrolactone with DMC.[43] More recently, Semak et al. also reported the synthesis of α-methyl-γ-butyrolactone by alkylation with DMC and K_2CO_3 at 210 °C.[44] Now, the possibility to develop this catalytic technology and apply it to biobased platform chemicals, has become of interest. Not only are dialkylcarbonates generally regarded as safe chemicals, but the byproducts of their reactions are CO_2 and the corresponding alcohol, both intrinsically easier to deal with than the salts originated by conventional alkylating agents (see above). These reactions involve simple, inexpensive, safe and readily available heterogeneous basic catalysts such as K_2CO_3, that can be filtered off at the end of the reaction and conveniently recycled. While the base is normally used in stoichiometric amounts to accelerate the reaction, and for easier recovery by filtration, nonetheless it was demonstrated here and elsewhere that it is a true catalyst.[45] It is noteworthy that DMC can be used both as reagent as well as reaction medium, implying that no additional solvent is required.

Herein we propose new options for the upgrading of four biobased lactones, with a view on obtaining alkylated derivatives and of demonstrating new chemical pathways for their catalytic transformation into new products. To this strategy we also couple the use of green chemical technologies as we consider that the use of chemical reagents derived from renewable resources must go hand in hand with greener reaction protocols in order to be truly sustainable. To this end, in the past two decades, dialkylcarbonates have been extensively studied for greener catalytic reactions from bulk industrial to lab scale chemistry.[46−48] The tunable reactivity and the low toxicity of dialkylcarbonates, particularly of lighter dimethyl- and diethyl-carbonate ($ROCO_2R$; R = Me, Et; DMC and DEC, respectively), have been key for their successful use as green reagents in place of hazardous reagents, such as phosgene and alkyl halides.[42] In this context, the reactivity of GBL, GVL, and DVL with organic carbonates ($ROCO_2R$; R = Me, Et, Bn) was examined under catalytic basic conditions. A simple array of new biobased products was obtained, some with excellent yields and selectivity.

EXPERIMENTAL SECTION

GBL, GVL, DVL, ECL, dimethylcarbonate, and diethylcarbonate were ACS grade and were employed without any further purification. Dibenzylcarbonate was prepared according to a recently reported method.[49] K_2CO_3 was stored under vacuum at 60 °C prior to use.

GC/MS (EI, 70 eV) analyses were run using a HP5-MS capillary column (30 m). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra at 101 MHz. Chemical shifts were reported in δ values downfield from TMS; $CDCl_3$ was used as solvent.

All reactions involving DMC and DEC were performed in stainless steel autoclaves with an internal volume of 120 or 220 mL, equipped with a pressure gauge, a thermocouple, and a magnetic stir bar. Heating was provided by means of an electric oven powered by a thermoregulator connected to the thermocouple.

Caution! *All the reported reactions generate endogenous pressure due to the formation of gaseous mixtures.* The final maximum observed pressure (syntheses of **1c** and **4c**) at 200 °C was 60 atm (10 atm observed once cooled to room temperature).

α,α-Carboxymethyl,methyl-γ-butyrolactone[50] (1b). GBL (2.00 g, 23.23 mmol) was loaded into an autoclave, together with DMC (29.40 mL, 348.47 mmol) as reagent/solvent and K_2CO_3 (3.21 g, 23.23 mmol). Once the autoclave was closed, air was purged by fluxing nitrogen through needle valves placed on the autoclave head. The mixture was then heated to reaction temperature (180 °C) and maintained under stirring (600 rpm) for the desired reaction time. After that the stirring was stopped while the autoclave was cooled down to room temperature and successively vented. DMC was removed under vacuum and $K_2CO_3$was filtered off. The compound **1b** was isolated after 3h through flash column chromatography on silica gel (gradient elution of petroleum ether and diethyl ether). Yield = 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.35 (m, 2H), 3.77 (s, 3H), 2,75 (ddd, 1H, J_1= 4.4 Hz, J_2= 7.0 Hz, J_3= 13.0 Hz), 2.18 (dt, 1H, J_1 = 8.4, J_2 = 13.2 Hz), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 175.7, 170.9, 65.8, 53.1, 49.8, 34.9, 20.2. Mass spectrum, *m/z*: 158 ([M]$^+$, <1%), 127 (5), 114 (13), 99 (33), 83 (42), 82 (36), 71 (13), 69 (20), 59 (32), 55 (100), 43 (30), 41 (64), 39 (67), 31(6).

α-Methyl-γ-butyrolactone[51] (1c). The reaction was set up and worked up as described for **1b**. After 24 h of reaction time at a temperature of 200 °C, **1c** was isolated through distillation under reduced pressure (bp 116−118 °C, 18 mmHg) with a yield of 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.34 (td, 1H, J_1 = 2.7 Hz, J_2 = 8.7 Hz), 4.18 (td, 1H, J_1 = 6.6 Hz, J_2 = 9.3 Hz), 2.60 (m, 1H), 2.43 (m, 1H), 1.92 (m, 1H), 1.29 (d, 3H, J = 7.1 Hz).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 180.2, 66.3, 34.2, 30.7, 15.2. Mass spectrum, *m/z*: 100 ([M]$^+$, 2%), 56 (38), 55(14), 42 (34), 41 (100), 39 (29).

α-Carboxyethyl-γ-butyrolactone (2a). The title compound was not isolated. Its spectroscopic data match those reported in the literature.[52]

α,α-Carboxyethyl,ethyl-γ-butyrolactone[53] (2b). The reaction was set up and worked up as described above. After 12 h of reaction time at a temperature of 200 °C, **2b** was isolated through flash column chromatography on silica gel (petroleum ether:diethyl ether = 1:1 as eluent). Yield = 28%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.32 (dd, J_1 = 5.4 Hz, J_2 = 8.9 Hz, 2H), 4.22 (ttd, J_1 = 3.6 Hz, J_2 = 7.4 Hz, J_3 = 10.8 Hz, 2H), 2.71 (m, 1H), 2.22 (td, J_1 = 8.8 Hz, J_2 = 13.1 Hz, 1H), 2.12 (qd, J_1 = 7.4 Hz, J_2 = 14.9 Hz, 1H),1.84 (qd, J_1 = 7.4 Hz, J_2 = 14.8 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 174.9, 169.6, 66.1, 62.1, 54.7, 31.2, 27.2, 14.0, 9.0. Mass spectrum, *m/z*: 186 ([M + 1]$^+$, 3), 158 (22), 141 (7), 130 (10), 127 (9), 114 (32), 113 (11), 112 (13), 99 (59), 97 (9), 96 (10), 95 (6), 85 (6), 83 (11), 81 (13), 69 (54), 68 (11), 67 (15), 55 (28), 54 (10), 53 (19), 45 (11), 43 (14), 42 (8), 41 (100), 39 (42), 30 (6).

α-Ethyl-γ-butyrolactone[54] (2c). GBL (2.00 g, 23.23 mmol) was loaded into an autoclave, together with DEC (33.80 mL, 278.97 mmol) as reagent/solvent and K_2CO_3 (3.21 g, 23.23 mmol). The reaction was then set up and worked up as already described. The product **2c** was distilled at reduced pressure together with the product **2d**. They were then separated through flash column chromatography on silica gel (diethyl ether:petroleum ether = 3:2 as eluent).Yield = 40%.^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):4.33 (td, J = 8.8, 3.1 Hz, 1H); 4.19 (td, J = 9.2, 6.7 Hz, 1H); 2.51−2.34 (m, 2H); 1.99−1.85 (m, 2H); 1.51 (ddq, J = 14.7, 8.6, 7.4 Hz, 1H); 1.00 (t, J = 7.5 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 179.1, 66.7, 40.8, 28.2, 23.6, 11.8. Mass spectrum, *m/z*: 114 ([M]$^+$, <1%), 113 (<1), 99 (1), 87 (4), 86 (89), 85 (8), 58 (6), 56 (20), 55 (100), 53 (7), 42 (51), 41 (39), 39 (23).

Diethyl Cyclopropane-1,1-dicarboxylate[51] (2d). The product **2d** was isolated from the same mixture as **2c**. After fcc, its yield was 8%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.19 (q, J = 7.1 Hz, 4H), 1.42 (s, J = 1.9 Hz, 4H), 1.27 (t, J = 7.1 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 170.0, 61.6, 28.5, 16.5, 14.3.170.0, 61.6, 28.5, 16.5, 14.3. Mass spectrum, m/z: 186 ([M]$^+$, 1%), 159 (20), 158 (21), 142 (8), 141 (100), 140 (6), 131 (6), 130 (41), 114 (21), 113 (63), 112 (56), 95 (12), 86 (22), 85 (14), 84 (7), 69 (10), 68 (12), 45 (8), 41 (17), 40 (21), 39 (20).

α-Benzyl-γ-butyrolactone[55] (3c). GBL (1.0 mL, 13.11 mmol), DBnC (3.49 g, 14.41 mmol) and K_2CO_3 (1.8 g, 13.1 mmol) were introduced in a round-bottomed flask equipped with a condenser. The stirred mixture was heated to 200 °C by an oil bath; after 12 h, the reaction was stopped, and the mixture was cooled down to room temperature. K_2CO_3 was filtered off and the crude was concentrated by rotary evaporator. Benzyl alcohol was then distilled at reduced pressure, and the oily residue was purified by flash column chromatography on silica gel (petroleum ether:diethyl ether:ethyl acetate = 4:1:1 as eluent). Compound **8a** was obtained in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39−7.15 (m, 5H), 4.23 (td, J = 8.8, 3.1 Hz, 1H), 4.14 (td, J = 9.3, 6.7 Hz, 1H), 3.25 (dd, J = 13.6, 4.0 Hz, 1H), 2.91−2.80 (m, 1H), 2.75 (dd, J = 13.6, 9.5 Hz, 1H), 2.30−2.20 (m, 1H), 1.99 (dtd, J = 12.8, 9.7, 8.6 Hz, 1H). Mass spectrum, m/z: 177 ([M + 1]$^+$, 7%), 176 ([M]$^+$, 59%), 149 (7), 148 (73), 147 (89), 131 (17), 130 (13), 117 (16), 115 (15), 104 (29), 103 (7), 92 (10), 91 (100), 78 (7), 77 (7), 65 (13), 51 (6).

α-Carboxymethyl-γ-valerolactone[51] (4a). The title compound was not isolated; its structure was confirmed by comparison with an authentic commercial sample.

α,α-Carboxymethyl,methyl-γ-valerolactone (4b). The title compound was not isolated. Its spectroscopic data match those reported in the literature.[56]

α-Methyl-γ-valerolactone[51] (4c). A mixture of GVL (2.00 g, 19.98 mmol), DMC (25.25 mL, 299.64 mmol), and K_2CO_3 (2.76 g, 19.98 mmol) was charged in a stainless-steel autoclave. The reaction was then set up and worked up as already described for **1b**. After 24 h at 220 °C, **4b** was isolated by distillation at reduced pressure (bp 102−103 °C, 70 mmHg). A mixture of diasteroisomers was obtained in a 82% yield. ^{1}HNMR (400 MHz, CDCl3) δ (ppm): 4.64 (m, 1H), 4.44 (m, 1H), 2,66 (m, 2H), 2.48 (m, 2H), 2.02 (m, 2H), 1.47 (td, 1H, J_1 = 10.4 Hz, J_2 = 12.2 Hz), 2.18 (td, 1H, J_1 = 8.4, J_2 = 13.2 Hz), 1.37 (d, 3H, J = 6.1 Hz), 1.33 (d, 3H, J = 6.4 Hz), 1.23 (d, 3H, J = 7.3 Hz), 1.22 (d, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm):180.0, 179.6, 74.9, 74.6, 39.1, 37.0, 36.3, 34.0, 21.0, 20.9, 15.7, 15.1. Mass spectrum, m/z: 114 (M$^+$, <1%), 99 (6), 71 (10), 70 (38), 55 (92), 43 (58), 42 (100), 41 (50), 39 (46).

α-Ethyl-γ-valerolactone[39] (5c). A mixture of GVL (2.00 g, 19.98 mmol), DEC (29.05 mL, 239.77 mmol) as reagent/solvent and K_2CO_3 (2.76 g, 19.98 mmol) was charged in a stainless-steel autoclave. The reaction was set up as and worked up as already described. After 72 h at 220 °C, **5c** was isolated by distillation at reduced pressure (bp 52−54 °C, 1.5 mmHg). A mixture of diasteroisomers was obtained in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.69−4.60 (m, 1H), 4.52−4.42 (m, 1H), 2.62−2.51 (m, 1H), 2.49−2.42 (m, 1H), 2.13−1.79 (m, 4H), 1.58−1.42 (m, 4H), 1.38 (dd, J = 18.3, 6.3 Hz, 6H), 0.99 (dt, J = 9.1, 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.1, 178.8, 75.0, 74.9, 42.9, 40.7, 36.4, 34.6, 23.8, 23.3, 21.3, 21.0, 11.7, 11.6. Mass spectrum, m/z: 128 ([M]$^+$ < 1%), 127 (1), 113 (14), 101 (6), 100 (100), 87 (3), 85 (4), 84 (5), 69 (25), 67 (8), 57 (8), 56 (51), 55 (62), 54 (5), 53 (5).

α-Benzyl-γ-valerolactone[57] (6c). A mixture of GVL (1.00 g, 9.99 mmol) DBnC (2.66 g, 10.99 mmol) as reagent/solvent and K_2CO_3 (2.76 g, 19.98 mmol) was set to react as already described for **3c**. The title compound was purified by flash column chromatography on silica gel (petroleum ether:diethyl ether:ethyl acetate = 4:1:1 as eluant). A mixture of diasteroisomers was obtained in a 65% yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 7.34−7.17 (m, 5H), 4.53−4.39 (m, 1H), 3.25 (ddd, J = 44.2, 13.9, 4.2 Hz, 1H), 3.02−2.85 (m, 1H), 2.74 (ddd, J = 28.1, 13.9, 9.6 Hz, 1H), 2.31 (ddd, J = 12.7, 8.4, 5.5 Hz, 1H), 2.13 (dt, J = 13.0, 7.5 Hz, 1H), 1.89 (ddd, J = 13.0, 9.1, 4.9 Hz, 1H), 1.61−1.48 (m, 1H), 1.34 (dd, J = 17.2, 6.3 Hz, 3H). Mass spectrum, m/z: 191 ([M + 1]$^+$, 3) 190 ([M]$^+$, 19), 149 (10), 148 (100), 147 (84), 131 (6), 118 (7), 117 (16), 115 (10), 91 (50), 77 (4), 65 (7), 55 (3), 51 (3).

Methyl 5-((Methoxycarbonyl)oxy)pentanoate (7a). A mixture of DVL (2.00 g, 19.98 mmol) DMC (25.25 mL, 299.64 mmol) as reagent/solvent and K_2CO_3 (2.76 g, 19.98 mmol) was charged in a stainless-steel autoclave. The reaction was then set up and worked up as already described for **1b**. After 4 h at 200 °C, **7a** was isolated by distillation at reduced pressure (bp 70 °C, 1.1 mmHg). Yield = 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (m, 2H), 3.74 (s, 3H), 3.64 (s, 3H), 2.32 (m, 2H), 1.69 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 173.4, 155.7, 67.4, 54.5, 51.4, 33.4, 28.0, 21.1. Mass spectrum, m/z: 190 ([M]$^+$, <1%), 159 (5), 115 (12), 114 (67), 113 (10), 101 (7), 99 (16), 83 (33), 82 (53), 77 (7), 74 (8), 73 (43), 72 (26), 71 (15), 59 (82), 58 (9), 57 (5), 56 (8), 55 (100), 54 (30), 45 (25), 43 (19), 42 (18), 41 (24), 39 (12).

Methyl-2-methyl 5-((Methoxycarbonyl)oxy)pentanoate (7c). A mixture of DVL (0.27 g, 2.69 mmol) DMC (3.40 mL, 40.35 mmol) as reagent/solvent and K_2CO_3 (0.37 g, 2.69 mmol) was charged in a stainless-steel autoclave. The reaction was then set up and worked up as already described. After 24 h at 200 °C, **7c** was isolated by flash column chromatography on silica gel (gradient elution, petroleum ether and diethyl ether). Yield = 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16−4.10 (m, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 2.51−2.42 (m, 1H), 1.78−1.63 (m, 3H), 1.51 (m, 1H), 1.16 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 176.6, 155.7, 67.7, 54.6, 51.5, 39.0, 29.8, 26.4, 17.0. Mass spectrum, m/z: 204 ([M]$^+$, <1%),173 (4), 129 (7), 128 (24), 115 (4), 113 (44), 100 (4), 97 (5), 96 (11), 88 (6), 87 (6), 85 (5), 77 (8), 73 (12), 70 (6), 69 (100) 68 (23), 67 (8), 59 (45), 57 (7), 55 (13), 45 (14), 43 (7), 42 (9), 41 (40), 39 (9).

Ethyl 5-((Ethoxycarbonyl)oxy)pentanoate (8a). A mixture of DVL (2.00 g, 19.98 mmol), DEC (36.30 mL, 299.64 mmol) as reagent/solvent and K_2CO_3 (2.76 g, 19.98 mmol) was charged in a stainless-steel autoclave. The reaction was then set up and worked up as already described. After 6 h at 200 °C, **8a** was isolated by distillation at reduced pressure (bp 81 °C, 0.8 mmHg). Yield = 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.23−4.09 (m, 6H), 2.36−2.29 (m, 2H), 1.76−1.67 (m, 4H), 1.27 (dt, J = 21.6, 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 173.1, 155.1, 67.2, 63.8, 60.3, 33.7, 28.1, 21.2, 14.2, 14.2. Mass spectrum, m/z: 218 ([M]$^+$, <1%), 129 (10), 128 (46), 101 (85), 100 (25), 99 (10), 91 (5), 87 (5), 83 (32), 82 (12), 73 (5), 72 (5), 69 (9), 63 (12), 60 (8), 59 (15), 58 (6), 57 (9), 56 (36), 55 (100), 54 (20), 45 (14), 44 (12), 43 (26), 42 (22), 41 (23), 39 (7).

Methyl 6-((Methoxycarbonyl)oxy)hexanoate (9a). A mixture of ECL (2.00 g, 17.52 mmol) DMC (22.14 mL, 262.80 mmol) as reagent/solvent and K_2CO_3 (2.42 g, 17.52 mmol) was charged in a stainless-steel autoclave. The reaction was then set up and worked up as already described for **1b**. After 6 h at 200 °C, **9a** was isolated by distillation at reduced pressure (bp 84 °C, 1.0 mmHg). Yield = 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ4.13 (t, J = 6.6 Hz, 2H), 3.76 (s, J = 5.4 Hz, 3H), 3.66 (s, 3H), 2.31 (t, J = 7.5 Hz, 2H), 1.72−1.60 (m, 4H), 1.45−1.35 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 173.5, 155.5, 67.5, 54.3, 51.2, 33.5, 28.1, 25.0, 24.2. Mass spectrum, m/z: 190 204 ([M]$^+$, <1%), 173 (7), 131 (8), 128 (39), 113 (22), 100 (14), 99 (9), 97 (39), 96 (27), 87 (36), 85 (6), 77 (20), 74 (92), 69 (86), 68 (100), 67 (18), 59 (72), 57 (8), 56 (8), 55 (83), 54 (8), 45 (30), 43 (28), 42 (20), 41 (57), 39 (20).

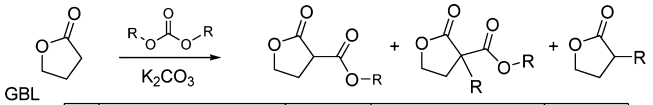
RESULTS

The reactions of γ-butyrolactone (GBL), γ-valerolactone (GVL), δ-valerolactone (DVL), and ϵ-caprolactone (ECL) with dimethylcarbonate or diethylcarbonate (DMC or DEC: bp of 90 and 126 °C, respectively) were carried out in sealed steel autoclaves, using the organic carbonate as reagent as well as solvent and potassium carbonate as the base. The choice of K_2CO_3 as base was dictated by our previous experience on these kinds of alkylation reactions and by its easy separation and recovery from the final reaction mixture. For dibenzylcar-

bonate (DBnC, bp = 180−190 °C at 2 mmHg), the reactions could be conducted using standard glassware. The reaction temperatures were chosen in the range 180−220 °C, and the reaction times between 12 and 72 h. The five-membered ring lactones GBL and GVL behaved similarly and are discussed together, while the six- and seven-membered lactones DVL and ECL are discussed separately.

Five-Membered Ring γ-Butyrolactone and γ-Valerolactone. *γ-Butyrolactone.* The products of the reactions of the five-membered GBL with three different dialkylcarbonates, in the presence of K_2CO_3 as catalyst, are summarized in Scheme 2.

Scheme 2. Products of the Base-Catalyzed Reaction of γ-Butyrolactone GBL with DMC, DEC, and DBnC



1	R = CH_3 (DMC)	**1a**	**1b**	**1c**
2	R = CH_2CH_3 (DEC)	**2a**	**2b**	**2c**
3	R = CH_2Ph (DBnC)	**3a**	**3b**	**3c**

GBL and DMC. In order to establish experimentally viable conditions for the base-catalyzed reaction between γ-butyrolactone and DMC, a range of reactions was run at 180 and 200 °C over different times. The results are summarized in Table 1.

At 180 °C, complete conversion of GBL was reached after 12 h (run 2) with a widely dispersed product distribution (**1a**:**1b**:**1c** = 14:30:35) accompanied by sizable amounts (20%) of unidentified byproducts. By raising the temperature to 200 °C complete conversion was achieved already after 6 h. In this case selectivity toward the methylated product **1c** appeared to become favored. By prolonging the reaction time to 20 h at 200 °C, selectivity toward products **1a** and **1b** decreased down to 0 and 13% respectively and a selectivity of 51% to **1c** was observed. Larger amounts of unidentified heavier products were however also observed (36%). The product distribution profile for the reaction of line 4 of Table 1 is shown in Figure 5. The graph indicates that **1a** and **1b** show intermediate-like behavior and that **1c** is the main product. **1c** was isolated from the reaction of line 4 of Table 1, with a final yield of 45%.

In order to confirm the catalytic nature of the reaction, an experiment was also run in the presence of substoichiometric amounts of K_2CO_3 (20% molar with respect to GBL). Under these conditions, 100% conversion was reached after 24 h, and

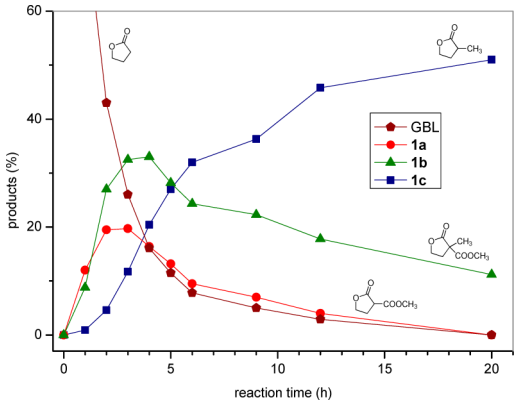


Figure 5. Reaction between GBL and DMC in the presence of K_2CO_3 at 200 °C.

products **1b** and **1c** were obtained with 22% and 64% selectivity, respectively (entry 5).

GBL and DEC. The reaction between γ-butyrolactone GBL and DEC was conducted under the same experimental conditions than with DMC. However, being the reaction slower in this case, higher temperatures were also tested. The results are listed in Table 2.

Table 2. Reactions of GBL with DEC in the Presence of K_2CO_3

				products (% GC)[b]			
run[a]	temp (°C)	time (h)	conversion[b] (% GC)	**2a**	**2b**	**2c**	others[c]
1	180	24	80	41	17	2	20
2	200	12	92	33	34	2	23
3	210	72	100	0	5	56	39
4	220	48	100	0	4	52	44

[a]All reactions were performed using a molar ratio GBL:DEC = 1:12 and GBL:K_2CO_3 = 1:1. [b]Conversion and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

At 180 °C, 80% conversion was reached after 24 h, with moderate (41%) selectivity toward the carboxymethylated product **2a**. At 200 °C almost quantitative conversion was achieved after 12 h with poorer selectivity (33 and 34% of **2a** and **2b** respectively), while at 210−220 °C, the selectivity toward **2c** was up to 52−56% at complete conversion (entries 3−4). Compound **2c** was isolated in a 45% yield.

Among major coproducts of the reaction between GBL and DEC (Table 2, entry 4), diethyl cyclopropane-1,1-dicarboxylate (**2d**) was isolated in a 8% yield. (Figure 6).

Table 1. Reactions of GBL with DMC in the Presence of K_2CO_3

					products (% GC)[b]			
run[a]	temperature (°C)	time (h)	GBL:K_2CO_3 (mol ratio)	conversion[b] (% GC)	**1a**	**1b**	**1c**	others[c]
1	180	3	1:1	76	38	33	1	4
2		12	1:1	99	14	30	35	20
3	200	6	1:1	99	4	28	39	28
4		20	1:1	100	0	13	51	36
5		24	1:0.2	100	0	22	64	14

[a]All reactions were performed using a molar ratio GBL:DMC = 1:15. [b]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

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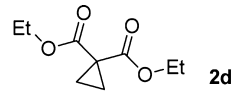


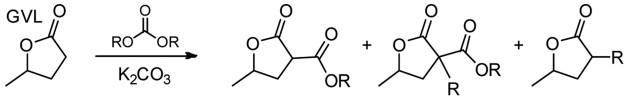
diethyl cyclopropane-1,1-dicarboxylate

Figure 6. Coproduct of the reaction between GBL and DEC.

GBL and DBnC. The reaction between GBL and DBnC was conducted at 200 °C for 12 h, using a molar ratio GBL:DBnC = 1:1.1 and GBL:K_2CO_3 = 1:1. A 90% gaschromatographic yield of **3c** was obtained. The purification of compound **3c** required distillation at reduced pressure followed by FCC. The product was isolated in 50% yield.

γ-Valerolactone. The products of the reactions of γ-valerolactone GVL with the three different dialkylcarbonates, in the presence of K_2CO_3, are summarized in Scheme 3.

Scheme 3. Products of the Base-Catalyzed Reaction of γ-Valerolactone GVL with DMC, DEC, and DBnC



4	R = CH_3 (DMC)	**4a**	**4b**	**4c**
5	R = CH_2CH_3 (DEC)	**5a**	**5b**	**5c**
6	R = CH_2Ph (DBnC)	**6a**	**6b**	**6c**

GVL and DMC. Based on the results with GBL, the reaction between γ-valerolactone and DMC was run directly at the higher temperatures of 200 and 220 °C (Table 3).

Table 3. Reactions of GVLwith DMC in the Presence of K_2CO_3

				products (% GC)[b]			
run[a]	temperature (°C)	time (h)	conversion[b] (% GC)	**4a**	**4b**	**4c**	others[c]
1	200	16	89	4	43	39	3
2		24	98	3	26	68	1
3		32	100	2	15	80	3
4	220	24	100	0	8	90	2

[a]All reactions were performed using a molar ratio GVL:DMC = 1:15 and GBL:K_2CO_3 = 1:1. [b]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

GVL reacted much more cleanly with DMC than GBL. At 200−220 °C, the conversion reached 100% after 32 and 24 h, respectively, with very high selectivity (80−90%) toward the monomethylated product **4c** (runs 3 and 4). Unidentified byproducts were in only 2−3% amount. The profiles of reaction conversion and product distribution vs time are shown in Figure 7.

The α-methylated product **4c** was distilled under reduced pressure and it was isolated in a 82% yield (purity >95%).

GVL and DEC. The K_2CO_3 catalyzed reaction between γ-valerolactone GVL and DEC was slower than with DMC. Table 4 describes the mixture compositions after different reaction times at 220 °C.

Selectivity toward **5c** increased with time, although at complete conversion byproducts started to ensue. After 72 h 71% of the ethylated product was observed along with 25% of

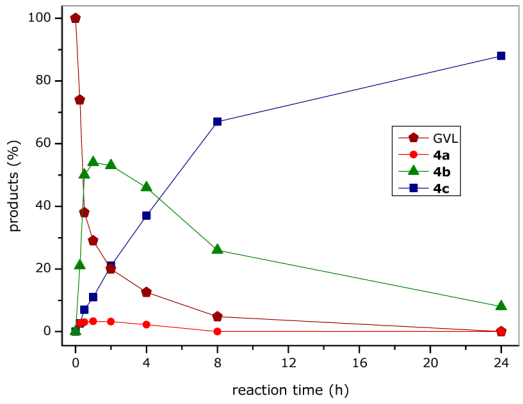


Figure 7. Reaction between GVL and DMC in the presence of K_2CO_3 at 200 °C.

Table 4. Reactions of GVL with DEC in the Presence of K_2CO_3

			products (% GC)[b]			
run[a]	time (h)	conversion[b] (% GC)	**5a**	**5b**	**5c**	others[c]
1	16	88	2	62	24	0
2	24	94	1	60	32	1
3	48	100	0	34	56	10
4	72	100	0	4	71	25

[a]All reactions were performed at 220 °C using a molar ratio GVL:DEC = 1:12 and GVL:K_2CO_3 = 1:1. [b]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

unwanted compounds. The α-ethylated product **5c** was distilled under reduced pressure and it was isolated in a 50% yield (purity >95%).

GVL and DBnC. The K_2CO_3 catalyzed reaction of GVL with dibenzylcarbonate took place cleanly at lower temperature (see Table 5).

Table 5. Reactions of GVL with DBnC in the Presence of K_2CO_3

					products (% GC)[b]	
run[a]	temperature (°C)	base (mol:mol)	time (h)	conversion[b] (% GC)	**6c**	others[c]
1	200	1	24	98	92	8
2		0.5	24	98	91	9
3	170	1	24	64	98	2

[a]All reactions were performed using a molar ratio GVL:DBnC = 1:1.1. [b]Conversion and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

After 24 h, and at 64% conversion, a selectivity of 98% was observed already at 170 °C. By raising the temperature to 200 °C conversion reached 98% with 92% selectivity toward the benzylated lactone **6c** after 24 h. Benzyl alcohol and dibenzyl ether were also observed in the reaction mixture (Scheme 4). No intermediate products were present.

Since the purification of compound **6c** required distillation at reduced pressure followed by FCC, it could be isolated in only a 65% yield (purity >98%).

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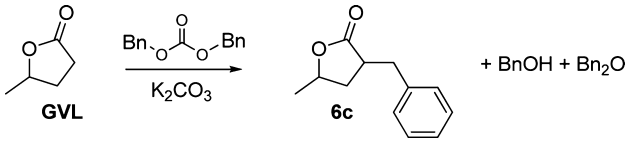
Scheme 4. Reaction of GVL with Dibenzylcarbonate



Six- and Seven-Membered Ring *δ*-Valerolactone and *ε*-Caprolactone. *δ-Valerolactone.* The products of the reactions of six-membered *δ*-valerolactone DVL with three different dialkylcarbonates, in the presence of K_2CO_3 as catalyst, are summarized in Scheme 5.

DVL and DMC. The K_2CO_3 catalyzed reaction of *δ*-valerolactone with DMC was initially performed on small scale (0.27 g, 2.69 mmol of substrate). Table 6 summarizes the results obtained running the reactions for different times at 200 °C. Molar ratios were the same as above: DVL:DMC = 1:15 and DVL:K_2CO_3 = 1:1

After 1 h conversion was already quantitative. The major component of the mixture was 4-(methoxycarbonyl)butyl methyl carbonate **7a** that derived from a ring-opening transesterification reaction. By prolonging the reaction time (as well as by increasing the temperature) sizable amounts of its *α*-methyl derivative **7c** were formed (see Scheme 5). The third major component was not isolated. However, it was identified as intermediate **7b** by GC-MS and ^{1}H NMR analyses of the crude mixture. MS spectra also suggested that byproducts labeled as others were most likely the 2-carboxymethyl-**7a** and *α*-methyl-DVL (Figure 8).

In order to monitor the reaction progress, a larger-scale reaction was set up and sampled at time intervals (see the Experimental Section). Figure 9 shows the profiles of the reactant DVL, and the major products **7a** and **7c**, respectively, over time. The reaction was slower than the ones of Table 6, due to the higher amounts involved. Nonetheless, the trend was consistent: the ring-opening transesterification product **7a** was obtained first (0–4 h, Figure 9); followed by the alpha methylation derivative **7c** (4–48 h, Figure 9).

Product **7a** was isolated in 80% yield from the reaction of Table 6, run 6, by distillation under reduced pressure (bp 70 °C at 150 Pa). Product **7c** was isolated in 44% yield from the reaction of Table 6, run 5, by FCC (see the Experimental Section).

DVL and DEC. The reaction of DVL with DEC was carried out under conditions similar to those used with DMC (Table 7). An analogous trend was observed: the ring-opening transesterification product **8a** was obtained first. It was then consumed in favor of **8c**. The overall process went through the intermediate **8b** (identified by GC-MS). Plausible byproducts were the corresponding ethyl-derivatives of compounds in Figure 8.

Table 6. Reactions of DVL with DMC in the Presence of K_2CO_3

run[a]	DVL (g)	time (h)	conversion[b] (% GC)	products (% GC)[b] 7a	7b	7c	others[c]
1	0.27	1	99	78	12	2	6
2		4	99	67	18	7	7
3		6	99	63	16	10	10
4		12	99	40	11	36	12
5		24	>99	18	5	64	13
6	2.00	4	99	94	3	>1	2
7		24	100	34	19	29	18

[a]All reactions were performed at 200 °C using molar ratios DVL:DMC = 1:15 and DVL:K_2CO_3 = 1:1. [b]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

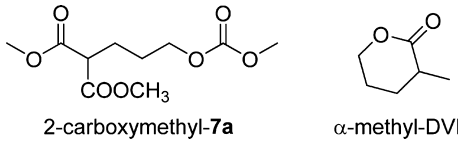


Figure 8. Plausible byproducts of the reaction between DVL and DMC.

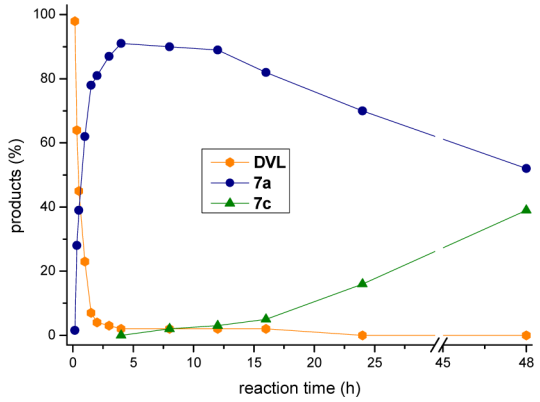
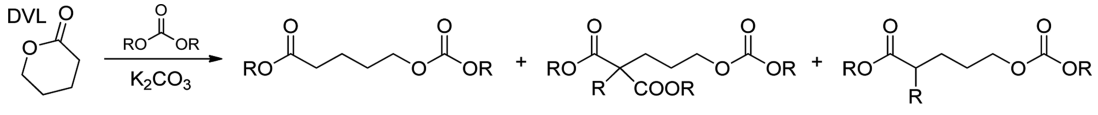


Figure 9. Reaction between DVL (4 g, 39.95 mmol) and DMC in the presence of K_2CO_3 as catalyst at 200 °C.

Product **8a** was isolated by distillation under reduced pressure (bp 81 °C at 0.8 mmHg) in 75% yield from the reaction of Table 7, run 2.

When the K_2CO_3 catalyzed reaction of DVL with DBnC was attempted, none of the above ring-opening or alkylation products were observed, rather DBnC was always present in the final reaction mixture, accompanied by BnOH and Bn_2O as side products. This led us to postulate extensive polymerization of DVL.[58]

Scheme 5. Base-Catalysed Reaction of *δ*-Valerolactone DVL with DMC and DEC



7	R = CH_3 (DMC)	**7a**	**7b**	**7c**
8	R = CH_2CH_3 (DEC)	**8a**	**8b**	**8c**

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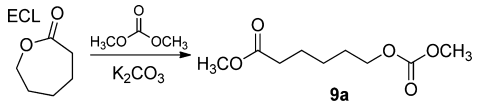
Table 7. Reactions of DVL with DEC Catalyzed by K_2CO_3

run[a]	DVL (g)	time (h)	conversion[b] (% GC)	products (% GC)[b] 8a	8b	8c	others[c]
1	0.27	6	100	53	25	5	17
2	2.00		97	90	5	>1	2

[a]All reactions were performed at 200 °C using molar ratios of DVL:DEC = 1:15 and DVL:K_2CO_3 = 1:1. [b]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [c]"Others" refers to products, the majority of which were not identified.

ε-Caprolactone. In order to confirm the reactivity observed for δ-valerolactone, the K_2CO_3 catalyzed alkylation reaction of the seven-membered ring ε-caprolactone was carried out with DMC. The reaction was performed on a 2.00 g (17.52 mmol) scale, using the same molar ratios as above (DVL:DMC = 1:15 and DVL:K_2CO_3 = 1:1), at 200 °C for 6 h. The observed product was methyl-6-((methoxycarbonyl)oxy)hexanoate **9a**, the analog of **7a** obtained previously for DVL (Scheme 6).

Scheme 6. Reaction of ECL with DMC



82% isolated yield

DISCUSSION

The K_2CO_3 catalyzed reaction of 5-membered ring lactones with dialkylcarbonates used as reagent and solvent proceeded to yield the α-alkylated homologues. The reaction pathway was similar to one reported elsewhere.[43] It involved three steps and consumed 2 mol of dialkylcarbonate $ROCO_2R$ per mole of lactone, as determined by previous investigations[59] and confirmed in our case by the intermediates observed in the reactions of γ-valerolactone and γ-butyrolactone. In the first step the carboxyalkyl derivative I_1 was formed by a $B_{AC}2$ (base catalyzed, acyl-oxygen bond breakage, 2 refers to the bimolecular nature) attack of the nucleophilic α-carbon of the lactone to $ROCO_2R$; in the second step the alkyl-carboxyalkyl derivative I_2 was formed by a $B_{AL}2$ reaction (base catalyzed, alkyl-oxygen bond breakage, bimolecular) with a second molecule of $ROCO_2R$; then, in the third and final step, decarboxylation afforded the α-alkylated lactone plus a third molecule of ROH (Scheme 7).

The reactions required relatively high temperatures in order to be practical: 200 °C for GBL with DMC and 220 °C for GVL with DMC. In the case of diethyl carbonate (DEC) a poorer reactivity was expected with respect to DMC: accordingly, the reaction was slower even at a higher temperature. Though, by prolonging the reaction up to 72 h, it was still possible to obtain good yields of the desired alpha-ethyl substituted lactone for both GBL and GVL. In analogy to previous findings,[60] a higher reactivity was observed for dibenzyl carbonate (DBnC): the reaction was much faster, possibly due to the activated benzylic position of the carbonate. No intermediate species were observed for DBnC, although these were still probably formed under the reported conditions. In all cases, the coproducts of the alkylation reactions were CO_2 and the corresponding alcohol ROH. Other possible by-products were the ethers (ROR) obtained by decarboxylation of the dialkylcarbonates, but these were ignored based on a previous investigation[61] where the extent of DMC decarboxylation was measured in the presence of different catalytic materials. At that time we observed that in the presence of K_2CO_3, after 6 h at 200 °C, the extent of DMC that was converted to the corresponding dimethyl ether was limited to 4%. The low extent of decarboxylation measured under the previously reported conditions prompted us to neglect this possible byproduct in the present investigation.

The reaction of the 5-membered ring lactones with the three carbonates DMC, DEC and DBnC could be pushed to yield the mono-α-alkylated products **1c−6c** with good to high selectivity (50−90%) and isolated yields (40−80%) as summarized in Table 8.

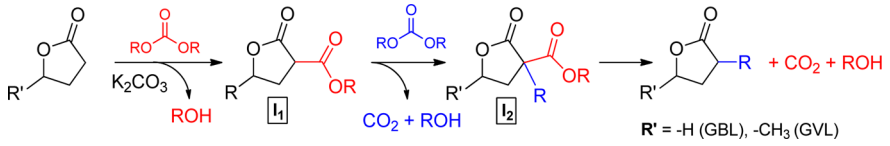
Table 8. Comparison between the Reactions of GBL and GVL

product	time (h)	conv[a] (%)	% (GC-MS)	yield[b] (%)	others[c] (%)
1c	24	100	51	45	38
2c	72	100	56	40	39
3c	12	100	88	50	12
4c	24	100	90	82	2
5c	72	100	76	50	16
6c	12	98	85	65	15

[a]Conversions and product percentages in the final mixture were determined by GC/MS analysis. [b]Isolated yield. [c]"Others" refers to products, the majority of which were not identified.

It should be highlighted that all the reported reactions were catalytic transformations. This was here further demonstrated una tantum by reacting GBL in the presence of a catalytic amount of K_2CO_3 (20 mol % with respect to GBL, entry 5 of Table 1) and observing that 100% conversion of the substrate was achieved, with 64 and 22% selectivity toward **1c** and **1b** respectively. In all the other cases, albeit used in stoichiometric amounts, K_2CO_3 acted as a catalyst. This was confirmed by the fact that in its absence the reaction was inhibited, that its presence accelerated the reaction, that it was not consumed, and that at the end of the reaction it could be recovered unchanged and filtered off to be reused. An accurate mass balance of recovered K_2CO_3 was not repeated here since previous work, as recent as 2012,[62] had indicated that its recovery was quantitative and its activity unchanged for successive cycles. Other authors have proposed methoxide (CH_3OK) as the active alkaline species for this transformation, formed in the reaction environment by disproportionation of

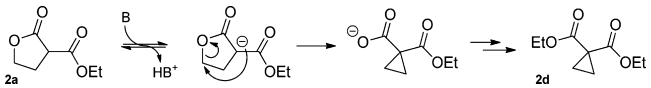
Scheme 7. Base Catalyzed Alkylation of 5-Membered Ring Lactones With Dialkyl Carbonate



K_2CO_3 in the presence of DMC at $T > 200$ °C.[44] Although this possibility is plausible, it should be noted that the nucleophilic activation of phenylacetonitrile by K_2CO_3 was observed previously at temperatures as low as 140 °C,[59] where the formation of methoxide is likely to be disfavored.

It was readily apparent that the reactions of GBL with DMC and DEC (products **1c** and **2c** of Table 8) suffered from the formation of byproducts. On the contrary the reactions of GVL were in general high yielding and selective. Our hypotheses to explain this different behavior were based on two facts. First, the inherent chemical stability of GVL due to its low ring strain[58] makes it likely less prone to parallel side reactions. Second, GBL is likely to undergo nucleophilic attack at the gamma as well as at the alpha positions. The higher reactivity of GBL and its easier ring-opening could therefore lead to a plethora of compounds. This was confirmed by some of the observed byproducts, the MS spectra of which suggested the formation of dimers. The observed side product **2d** shown in Figure 6 also lends support to this analysis: the formation of **2d** can be explained by ring contraction of intermediate **2a** obtained via intramolecular nucleophilic attack as shown in Scheme 7. This cyclization can be classified as *3-exotet* according to Baldwin[63] and is therefore favored (Scheme 8).

Scheme 8. Hypothesis of Mechanism for 2d Formation



GVL on the other hand reacted very cleanly and selectively with dialkylcarbonates, especially DMC. The methyl group protects the gamma position from further reactions, and directs the selectivity toward the alpha attack. Interest in this renewable lactone, coupled with the use of a safer greener reagent such as DMC and of a catalytic protocol, exemplify in our view a pathway toward the development of a truly sustainable reaction.

Six- and seven-membered ring DVL and ECL were subjected to the same reactions as the other lactones, but the outcome was markedly different. Rather than giving alpha-alkylated lactones, both these substrates underwent a ring-opening reaction that yielded highly oxygenated acyclic products **7a**, **8a**, and **9a**, bearing an ester and a carbonate group at each end. In our hypothesis, ring opening of DVL and ECL was favored by the presence of traces of water (path I, Scheme 8). The open compound reacted then twice with DMC, releasing methoxide, which could in principle continue ring-opening via the second pathway (II) shown in Scheme 9.

This ring-opening behavior was due to the higher reactivity of the six- and seven-membered ring lactones respect to the five-membered ones,[64] as confirmed also by the fact that DVL and ECL are widely used monomers for ring opening polymerization. In this context it is worth underlining that DVL transforms into linear polyesters merely on storage at room temperature.[58] Therefore, a reaction such as the one here described that allows to trap DVL and ECL in a monomeric form may provide a useful synthetic perspective, particularly in view of the high oxygen content of product **7a** and **9a**. It should also be noted that few examples exist in the literature in which a carbonate formally acts as an oxidant.[65] While ring-opening of DVL was extremely fast, still traces of α-methyl DVL were observed in the reaction mixture by GC-MS, thus confirming the reactivity of organic carbonates with lactones. Ring-opened products **7a** and **8a** reacted further with DMC under the present alkaline conditions and formed the alkylated products **7c** and **8c** analogously to what was observed in previous studies.[43]

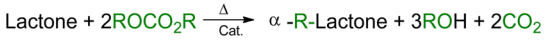
CONCLUSIONS

This work highlights potential upgrading pathways of four lactones (GBL, GVL, DVL, ECL) obtainable from a renewable biorefinery scheme, by using a set of green and safe compounds such as dimethyl-, diethyl-, and dibenzylcarbonates and catalytic reactions. Carbonates not only displayed a double reactivity as alkylating and carboxyalkylating agents of lactones, but they also served as solvents. Accordingly, in the presence of K_2CO_3 as a base, the product distribution of the investigated reactions could be tuned by variations of temperature and time. Based on kinetic profiles, some insight is obtained as to the reaction mechanisms.

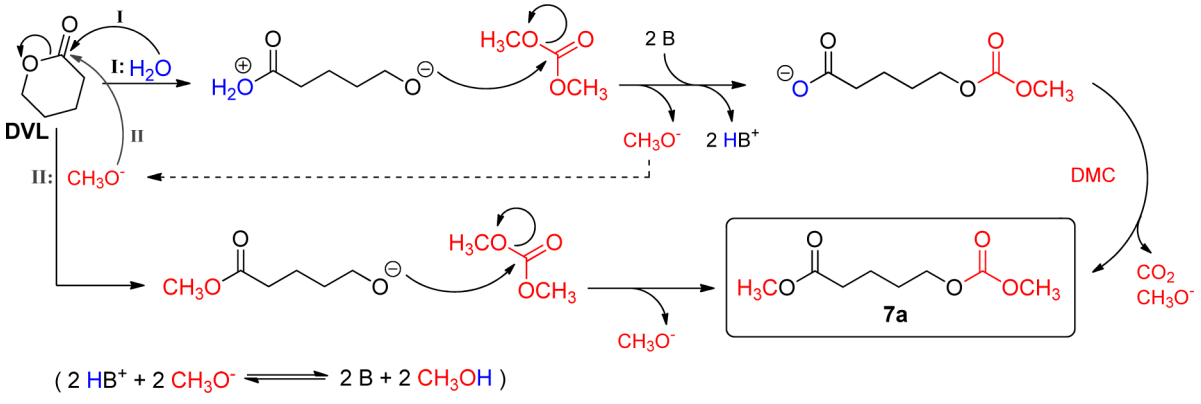
The overall balance of the reaction yields one mole of α-alkyl-lactone, three of alkyl-alcohol and two of CO_2 starting from 1 mol lactone and 2 mol dialkyl carbonate (Scheme 10). The alcohol can in principle be reused to synthesize the starting carbonate, and K_2CO_3 is recovered unchanged at the end of the reaction.

Scheme 10. Overall reaction for the alkylation of lactones

Overall reaction:



Scheme 9. Hypothesis of Mechanism for the K_2CO_3 Catalyzed Reaction between DVL and DMC



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Finally, heterogeneous catalysis itself represents one of the strongholds of green chemistry as it allows to intensify the process, reduce the energy demand, improve selectivity, and accelerate reaction rates. In this context, the catalyst used (K_2CO_3) is a safe and easily recoverable and recyclable compound. Moreover, in perspective, the overall procedure is perfectly suited to be intensified by moving to continuous flow catalytic conditions. The intrinsic value of these kinds of transformations can therefore epitomize a green AND sustainable processes toward new biobased chemicals.

■ ASSOCIATED CONTENT

Supporting Information

Full spectral characterization of all compounds (^{1}H NMR, ^{13}C NMR, heterocorrelated ^{1}H−^{13}C NMR, MS). This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*alvise@unive.it.

Notes

The authors declare no competing financial interest.

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